

Electronic structure and magnetic anisotropy of the $[\text{Co}_4(\text{hmp})_4(\text{CH}_3\text{OH})_4\text{Cl}_4]$ molecule

Tunna Baruah ^a and Mark R. Pederson ^{* b}

^aDepartment of Physics, Georgetown University, Washington, DC 20057, USA

^bCenter for Computational Materials Science, Code 6392, Naval Research Laboratory Washington, DC 20375-5000, USA

Accurate density-functional based calculations have been performed on the $\text{Co}_4(\text{hmp})_4(\text{CH}_3\text{OH})_4\text{Cl}_4$ molecular magnet where hmp is deprotonated hydroxymethyl pyridine. In addition to the experimentally observed staggered geometry, we identify two isomers, referred to as eclipsed and half-staggered/half-eclipsed, that are reasonably low in energy. Our calculations show that the magnetic anisotropy is strongly dependent on the pyridine-pyridine separation and that the three structures exhibit easy axis, easy plane and triaxial behavior. Other effects such as partial reprotonation of the hmp is considered.

The magnetic molecules containing transition metal atoms are being widely studied due to potential technological applications for information storage and quantum computing [1]. The magnetic molecules show magnetic hysteresis behavior reminiscent of single domain magnets and exhibit the phenomenon of quantum tunneling of magnetization. Observation of such behavior in a molecular magnet is greatly facilitated by a reasonably high net spin and a large magnetic anisotropy energy (MAE). A very recent experimental report of a single molecule magnet consisting of $\text{Co}_4(\text{hmp})_4(\text{CH}_3\text{OH})_4\text{Cl}_4$ where hmp- is the deprotonated hydroxymethylpyridine, suggests that this molecule is quite promising since the magnetic anisotropy energy per transition metal atom is high (25-50K) [2] compared to other magnetic molecules $\text{Fe}_8\text{-tacn}$ [3], $\text{Mn}_{12}\text{-acetate}$ [4,5,6,7] where it is (3-6K). The reported ferromagnetic ordering of the Co_4 molecule also differs qualitatively from the ferrimagnetic spin ordering observed in the Mn_{12} and Fe_8 . The negative anisotropy energy for a transition metal with more than 5 d electrons is also considered to be unusual.

In order to gain more insight into the prop-

erties of this molecule, we have carried out a detailed *ab initio* study of the electronic structure and magnetic anisotropy energy of $[\text{Co}_4(\text{hmp})_4(\text{CH}_3\text{OH})_4\text{Cl}_4]$ for different conformers. Density functional theory [8,9] based all-electron, spin-polarized calculations were carried out with the NRLMOL code [10,11] within the generalized gradient approximation to the exchange-correlation functional [12].

In the experimentally obtained Co_4 cluster [2], the four cobalt atoms in the molecule are bonded to organic hydroxy-methyl-pyridine(hmp) ligands (Fig. 1(a)). The four Co(II) atoms and the four oxygens from the CH_2O^- radicals of the hmp ligand form an inner cubane structure. The experimentally observed molecule exhibits S_4 point group symmetry and is made up of four units where each 22-atom unit (Fig. 1(b)) consists of Co^{+2} , Cl^- , CH_3OH and the hmp^- ligand. An eclipsed geometrical isomer (Fig. 2(a)) can be generated by continuously distorting the lower half of the staggered experimental geometry or from the inequivalent 22-atom complex from the group of order 4 generated from $(xyz) \rightarrow (-x, -y, z)$ and $(xyz) \rightarrow (y, x, -z)$. Another energetically competitive structure (Fig. 2(b)), which we refer to as half staggered and half eclipsed (HSHE), can be generated by rotating and appropriately reorienting only the Cl and ligands on the lower

*Corresponding author: FAX: +1-202-404-7546; e-mail: pederson@dave.nrl.navy.mil

half of the experimental structure. This structure has one symmetry operation $[(xyz) \rightarrow (x, -y, -z)]$. Complete geometry optimizations were carried out for each conformer.

The starting parameters for the experimentally reported staggered geometry were taken from the reported isostructure of the $[\text{Ni}_4(\text{hmp})_4(\text{CH}_3\text{OH})_4\text{Cl}_4]$ [13] molecular crystal. Upon relaxation, the volume of the molecule increases due to the repulsion of the hmp ligands in parallel positions. The eclipsed structure was found to be higher in energy than the staggered structure by 2.77 eV. Since this energy difference is probably due to intraplanar and interplanar steric repulsions, we have been motivated to look at the half-staggered and half-eclipsed geometry as well. We find that the relaxed HSHE geometry is only 0.79 eV above the experimental geometry. The cohesive energy was found to be approximately 4.7 eV/atom for all structures.

The spin-projected total density of states (DOS) as well as the Co *d* density of states of the staggered structure are shown in Fig. 3. The Fig. 3 clearly shows that the states near the Fermi level arises mainly from the Co atoms. These states also contain minor contributions from the oxygen and chlorine atoms. The Co *d* majority states are fully occupied. The figure shows that both the HOMO and the LUMO belongs to the minority spin Co *d* levels which is true in all the structures. The minority gap in the staggered structure is 0.55 eV. A smaller gap leads to a higher value of the magnetic anisotropy energy. The gap is found to be highly sensitive to the orientation of the ligands.

The spin-density in a sphere of radius 2.6 a.u. around each Co atom shows that Co atoms have a local moment of $3 \mu_B$ which is also expected from electron counting considerations. This leads to a ferromagnetic structure with a total moment of $12 \mu_B$ (or $S=6$) for all isomers and is in agreement with experiment [2]. Therefore, the orientation of the hmp ligands does not affect the magnetic moment. An isolated Co_4O_4 cubane is also found to possess a magnetic moment of 12. Our investigation on the effect of hydrogen dopants shows that the inclusion of additional hydrogens leads to a partial reprotonation of the cubane OC-CH_2

groups and insertion of the electrons into the vacant minority Co_{3d} states just above the Fermi level. This reduces the magnetic moment by $1 \mu_B$ per hydrogen atom.

Our calculations have shown that the states near the Fermi level are dominated by the cobalt *d* states with both the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) belonging to the minority spin Co *d* levels. The HOMO-LUMO gap in the staggered structure is 0.55 eV. The gap is found to be highly sensitive to the orientation of the ligands. In the eclipsed structure, the HOMO-LUMO gap is small (0.09 eV), while for the HSHE structure, it is 0.41 eV. This leads to interesting magnetic behavior in the three structures. The values of the gap and the MAE of the three conformers are summarized in Table 1.

The lowest order spin hamiltonian for a single molecular magnet can be modelled as

$$H = DS_z^2 + E(S_x^2 - S_y^2) + g\mu\vec{B} \cdot \vec{S}$$

where D and E are the second-order axial and transverse anisotropies. \vec{B} and g are the applied magnetic field and the Landé g -factor, respectively. The main contribution to the second-order anisotropy energy arises from the spin-orbit coupling. The effect of the spin-orbit coupling and the second-order anisotropy energy was calculated here using the second-order perturbative treatment presented in Ref. [14]. We also used an alternative treatment given in Ref. [15] where the principal axes and anisotropy energies may be determined by diagonalizing the anisotropy tensor. While the experimental staggered structure with S_4 symmetry is uniaxial, (i.e. $E=0$ by symmetry) the other two structures will have a transverse component (E).

The calculated magnetic anisotropy energy of the uniaxial, optimized staggered structure was found to be 23 K although the initial structure, based on experimental parameters, showed a high value of MAE of 57 K. The separation between pyridine rings was found to increase upon optimization which in turn increased the HOMO-LUMO gap. The HOMO-LUMO gap for the initial geometry of the experimental structure was found to be 0.09 eV. This observation opens up an

exciting possibility of altering the MAE by manipulating the pyridine-pyridine separations, in particular, by the application of pressure. It may be mentioned here that Yang et al. [2] have established that the magnetization barrier is ~ 100 -200 K. The large discrepancy between the theoretical and experimental values further supports the possibility that the MAE may exhibit significant pressure dependencies. So crystal packing effects may play an important role here.

The eclipsed structure, on the other hand, shows a more promising magnetic behavior (Table 1). In this case, the magnetization has easy, medium and hard axes. The easy axis lies along the axis of the molecule as in the experimental structure. The energy barrier between the easy and the medium axes is 95K while that between the medium and hard axes is 65K. This leads to a rather large D parameter of -3.55K and an E parameter of -0.91K. Interestingly, the MAE of the HSHE structure (50K) lies between the MAE of the staggered and the eclipsed structures. However, this geometry has an easy plane of magnetization. Thus, changing the orientation of the ligands significantly, albeit indirectly, influences the magnetic behavior of the Co_4 through band gap changes.

One possible way of achieving an overall easy axis is through the orthogonal hard axis alignment model in which each cobalt exhibits a local easy plane and the intersection of easy planes between the lower and upper Co atoms determines an easy axis [2]. Another way is for each atom to exhibit a local easy axis along the global uniaxis. Within the second-order perturbation theory, and the LCAO method used here, it is possible to decompose the anisotropy hamiltonian into a sum of 4-center terms by expanding the relevant matrix elements into their atomic constituents. Because the Co d states are localized and dominate the behavior near the Fermi level, one expects that the single-center diagonal terms will be primarily responsible for the anisotropy energy. We have determined numerically that this is an excellent approximation and find that in all structures, the local alignments are identical with the local hard axis lying along the in-plane Co-O bond in the cubane (Co and O are attached to two paral-

lel hmp ligands) and the local medium axis lying along the Co-N bond (Fig. 4). This leads to the situation where the local hard and easy axes lie on a plane bisecting the molecule. For the case of the staggered structure, the local hard axes of the upper and lower Co atoms are orthogonal, which leads to the global easy axis lying along the axis of the molecule. In the other two structures, the local hard axes are aligned parallel and the competition between the medium and the local easy axes leads to a triaxial alignment in one and to an easy plane of alignment in the other. For the latter, the easy and the medium axes are nearly degenerate.

In conclusion, we show that the magnetization of the Co_4 molecule varies strongly with the orientation of the various ligands. While the staggered and eclipsed structures have a preferred axis of magnetization, the intermediate structure has a preferred plane of magnetization. For the higher energy isomer, the energy barrier between the hard and the medium axis is quite high (~ 95 K). This is especially interesting in view of the small number of transition metal atoms in the molecule. Our results suggest that the anisotropy energy may be strongly varied by manipulating the pyridine-pyridine spacing and ligand orientation. Determining a means for constraining the ligands by either chemical, physical or electrostatic means would be a worthwhile investigation.

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Table 1

The magnetic moment(μ), HOMO-LUMO gap (Δ), magnetic alignment energies, with respect to the easy axis, and type of magnetic alignment of the three different structures of the Co_4 molecule. H and M correspond to hard and medium axes respectively. S, E and HSHE pertain to staggered, eclipsed and half-staggered/half-eclipsed structures respectively.

Struc.	μ	Δ (eV)	Energy (K)		Type
			H	M	
S	12	0.55	23	23	Easy axis
E	12	0.09	160	95	Triaxial
HSHE	12	0.41	50	10	\sim Easy plane

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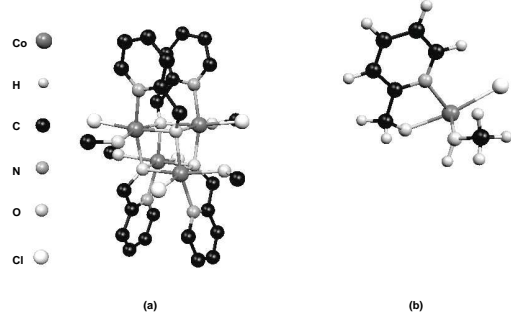


Figure 1. (a) The geometry of the lowest-energy staggered structure in which the hydrogen atoms are not shown. (b) The inequivalent building block of each molecule which consists of the Co^{2+} , Cl^- , CH_3OH and the hmp^- ligands.

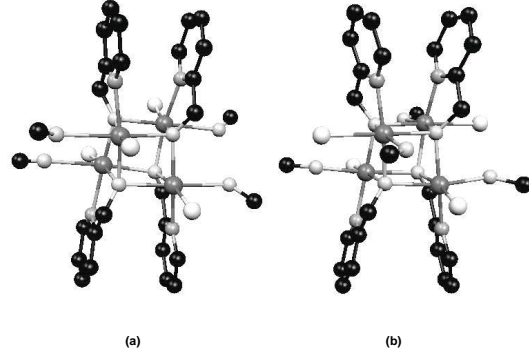


Figure 2. The optimized (a) eclipsed and (b) half-staggered half-eclipsed geometries in which the hydrogen atoms are not shown.

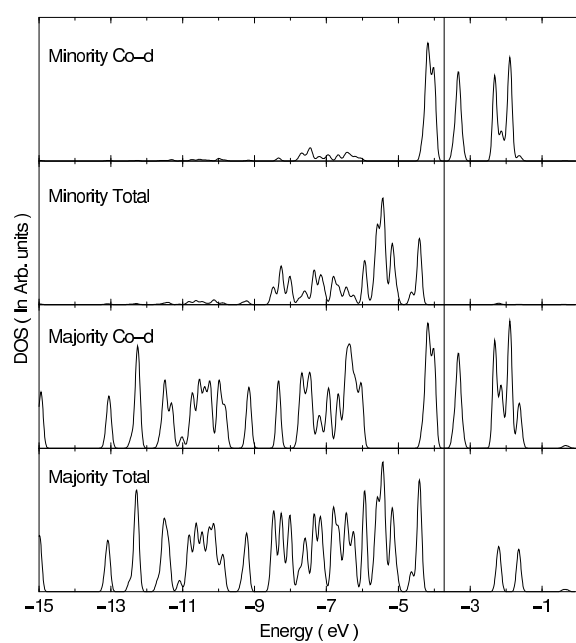


Figure 3. The total and Co-d majority and minority spin density of states of the staggered Co_4 molecule.

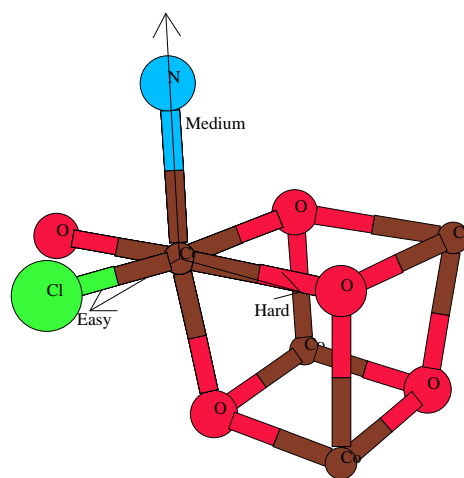


Figure 4. The local easy, medium and hard axes on a representative Co atom. Only the cobalt-oxygen cube part of the whole molecule is shown.